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# Dihydride formation in the reaction of water with Si(111)-(7×7)

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The reaction of water with Si(111)-(7×7) was studied at 80 K using a scanning-tunneling microscope (STM) and electron energy-loss spectroscopy (EELS). Two-dimensional islands of depressed Si adatoms were observed in topographic STM images, which was ascribed to the bonding with dissociated OH species. The island formation is not consistent with the previously proposed reaction mechanism that the adatom-rest atom pair acts as a bond cleaver and half of the adatoms remain intact in the half unit cell. Based on the result of EELS, we modify the mechanism and propose that dihydride species is formed at the rest-atom site, enabling more than half of the adatoms to be reacted.

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## I. INTRODUCTION

Water has been used as a reactant to oxidize silicon surfaces, and its initial-reaction process has attracted attention not only from fundamental interests but from a field of microelectronic material. Numerous studies have been performed, thus far, to elucidate the reaction process on a Si(111)-(7×7) surface,<sup>1,2</sup> and it is now established that water adsorbs dissociatively at room temperature, forming Si-H and Si-OH species.<sup>3,4</sup>

Figure 1 depicts a (7×7) reconstructed Si(111) surface.<sup>5</sup> There exist four inequivalent topmost atoms (adatoms) with dangling bonds, namely, center and corner adatoms on faulted and unfaulted halves. The “faulted” refers to a stacking fault of the adatom layer with respect to the fourth layer. The second layer has two inequivalent atoms (rest atoms) with dangling bonds on faulted and unfaulted halves. Note that each center adatom has two neighboring rest atoms, whereas the corner adatoms have one. Avouris and Lyo<sup>6</sup> first employed a scanning-tunneling microscope (STM) to investigate microscopic reaction process of water on Si(111)-(7×7) at room temperature. Si adatoms appeared as depression in topographic images, suggesting that dangling bonds of Si adatoms were passivated by OH or H species. The center adatoms preferentially reacted with water by a factor of ~2 to the corner adatoms. The preference factor of nearly two implied that dissociation proceeds across an adatom-rest atom pair within a half unit cell, since the center adatoms have twice as many neighboring rest atoms as the corner adatoms.

However, such a simple model of adatom-rest atom pair reaction was questioned by Self *et al.*<sup>7</sup> If the reaction occurred across the adatom-rest atom pairs, it should saturate with 50% of total adatom intact, since the number of the rest atoms (three) is only half of that of the adatoms (six) in the half unit cells. On the contrary, they observed that 69% of adatoms were reacted at 300 K, and proposed that the adatom-rest atom-pair mechanism is an incomplete description of the reaction.

The adsorption sites of the dissociated OH and H fragments are also controversial. Theory<sup>8</sup> and scanning-tunneling spectroscopy<sup>9</sup> indicated that rest atoms act as electron donors

due to its excess charge, whereas adatoms do as electron acceptors. Thus, it is expected that lone pairs of water initially interact with an electron-deficient adatom, followed by dissociation, and the OH and H fragments bond to the adatom and adjacent rest atom, respectively. On the other hand, an opposite bonding configuration was shown to be favored in terms of the total-energy calculation.<sup>10</sup>

At lower temperature (100 K), the reaction was studied using electron energy-loss spectroscopy (EELS),<sup>3</sup> although there exists no report from microscopic point of view in the literature. In this work, we studied the reaction of water with a Si(111)-(7×7) surface at 80 K by means of STM and EELS. Reacted sites form two-dimensional islands on the surface, which is not consistent with the model of adatom-rest atom pair reaction. Vibrational spectra revealed presence of dihydride species, and thus, we propose that the dissociative reaction across the adatom-rest atom pairs proceeds with the formation of dihydride species at the rest-atom sites.

## II. EXPERIMENTAL

An STM (USM 604, UNISOKU) is housed in an ultrahigh-vacuum (UHV) chamber with the base pressure be-

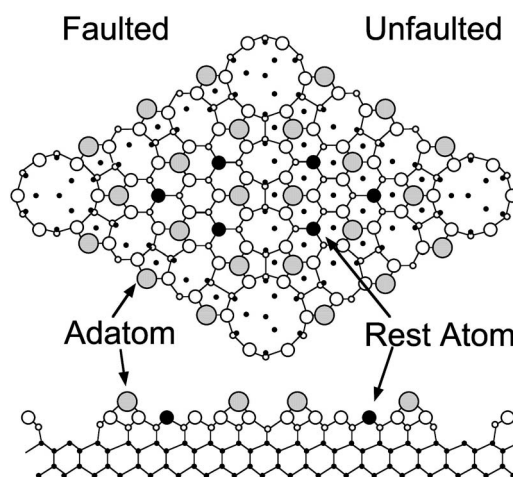


FIG. 1. Schematic structure of the Si(111)-(7×7) unit cell. The unit cell consists of faulted and unfaulted half cells, each of which involves six adatoms and three rest atoms.

low  $5 \times 10^{-11}$  Torr. The STM images were acquired in constant current mode at 78 or 300 K with an electrochemically etched tungsten tip. The images were obtained with a constant tunneling current of 0.2 nA. The EELS experiments were conducted in a separate UHV chamber equipped with a high-resolution electron energy-loss spectrometer (LK-5000, LK Technologies, Inc.) and a four-grid retarding-field analyzer for low-energy electron diffraction (LEED). The base pressure of the chamber was below  $8 \times 10^{-11}$  Torr. The primary electron energy was 7.3 eV, and both incidence angle and reflection angle were  $60^\circ$  from the surface normal. The scattering plane was aligned along the  $[01\bar{1}]$  direction. All measurements were conducted at 82 K, and typical energy resolution (full width at half maximum of the elastic peak) was 3 meV.

The silicon used in the experiments was cut from a *n*-type, As-doped, 0.004  $\Omega$  cm wafer, which was cleaned by the overnight degassing at  $\sim 900$  K, followed by flashing up to  $\sim 1500$  K. The prepared surface showed  $<0.3\%$  adatom defects in STM image. A sharp  $(7 \times 7)$  LEED pattern was observed, and EELS showed no trace of impurities. The sample was exposed to  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  gasses via tube dosers, which were positioned  $\sim 1$  cm apart from the sample surface. Exposures were given by the background water pressure multiplied by time in units of L (1 L =  $1 \times 10^{-6}$  Torr s). The actual exposure was larger than indicated due to the use of dosers. The doser magnification factors were roughly estimated to be  $\sim 8$  for both STM and EELS experiments. The adatom coverage  $\theta_{ad}$  is defined as the ratio of the number of reacted adatoms to that of the total adatoms.

### III. RESULTS

Typical STM images of  $\text{Si}(111)-(7 \times 7)$  exposed to  $\text{D}_2\text{O}$  at 78 K are shown in Fig. 2. Similar results were obtained with  $\text{H}_2\text{O}$  exposure. Reaction products at the initial stage (0.01 L) are shown in Fig. 2(a), where the adatoms appear dark and form two-dimensional islands. The darkened areas are frequently accompanied with unstable features due to tip-surface interaction. At higher exposures (0.1 L), the unstable features become more significant. After several cycles of scans, the tip-surface interaction results in anisotropic dark regions as shown in Fig. 2(b). Note that the area was scanned from left to right. The interaction cannot be excluded even though the lowest tunneling current 15 pA was applied.

On the other hand, stable imagings were enabled after the surface was heated to 300 K, as shown in Figs. 2(c) and 2(d), where the exposure before heating was the same as for Figs. 2(a) and 2(b), respectively. In the reacted area, all adatoms appear to be involved in the reaction (locally  $\theta_{ad}=1$ ). These results are not consistent with the proposed reaction mechanism that water dissociates across the adatom-rest atom pairs, and thus, half of the adatoms remains intact ( $\theta_{ad}<0.5$ ).

In comparison, STM images of  $\text{Si}(111)-(7 \times 7)$  exposed to  $\text{D}_2\text{O}$  at 300 K are shown in Figs. 3(a) and 3(b) with  $\theta_{ad}=0.156$  and  $\theta_{ad}=0.316$ , respectively. Similar results were obtained with  $\text{H}_2\text{O}$  exposure. The reaction proceeds uni-

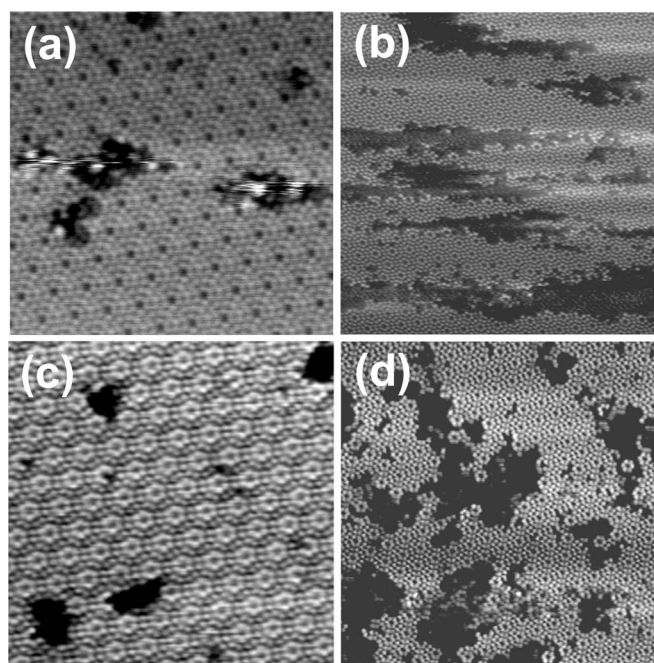


FIG. 2. (a) An STM image of  $\text{Si}(111)-(7 \times 7)$  exposed to 0.01 L  $\text{D}_2\text{O}$  at 78 K ( $270 \times 270 \text{ \AA}^2$ ). The sample bias was 1.5 V. (b) An STM image obtained after exposed to 0.1 L  $\text{D}_2\text{O}$  at 78 K and several scans from left to right ( $500 \times 500 \text{ \AA}^2$ ). The anisotropic dark region indicates the tip-induced reaction. Other conditions are same as (a). The surfaces (a) and (b) were heated to 300 K and then were imaged at 78 K in (c) and (d), respectively (different regions). The scan sizes of (c) and (d) were  $270 \times 270 \text{ \AA}^2$  and  $500 \times 500 \text{ \AA}^2$ , respectively. The sample bias was (c) 1.9 V and (d) 1.7 V.

formly compared to the case at 78 K, and the reaction preference of the center adatom was observed with respect to the corner adatom by a factor of 2–4, while no preference was found for the two different half unit cells, which is consistent with the previous results.<sup>6,7</sup> At 300 K, the majority of the reacted adatoms is compatible with the adatom-rest atom-pair reaction model, although 3% of the reacted adatoms in Fig. 3(a) cannot be explained by the model (depicted by the asterisk). Percentages of the reacted adatoms that are not compatible with the model are shown in Fig. 3(c) as a function of  $\theta_{ad}$ . The result shows that the model fails even at 300 K as previously pointed out.<sup>7</sup>

The island formation at 78 K suggests a presence of attractive interaction between the reactants. Although it is not prominent at 300 K, the reaction occurs preferentially at the adjacent site of the already reacted adatom. The numbers of the reacted sites per 100 unit cells are shown in Fig. 3(d) as a function of the number of the neighboring reacted adatom. The solid circles and squares are the results of the experiment and calculation, respectively, at  $\theta_{ad}=0.156$ , and more than 1000 unit cells were investigated. In the calculation, we assumed that the reaction proceeds with no correlation between the reactants. The neighboring sites were defined as (i) center-center adatoms, (ii) center-corner adatoms within a half unit cell, and (iii) corner-corner adatoms, (iv) center-center adatoms between different halves. The average numbers of the neighboring reacted adatoms are 1.26 and 0.72 at



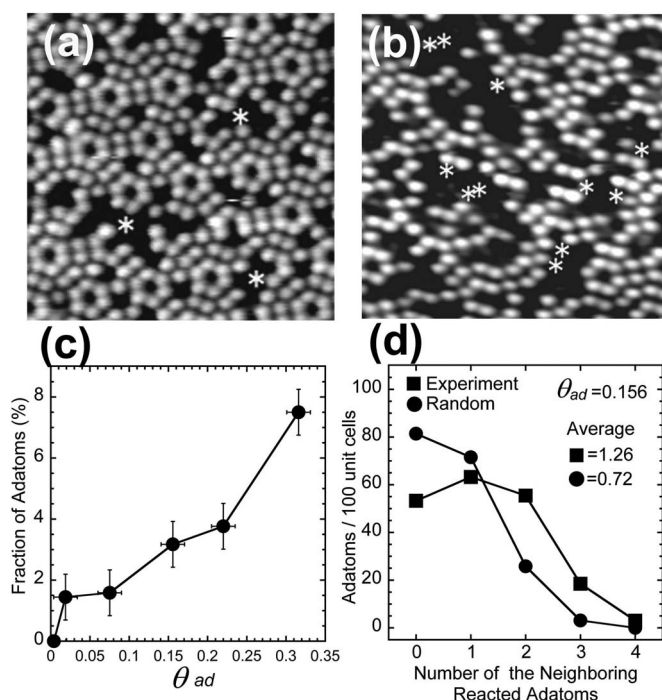


FIG. 3. (a) An STM image of Si(111)-(7 $\times$ 7) exposed to 0.07 L D<sub>2</sub>O at 300 K (135 $\times$ 135 Å<sup>2</sup>).  $\theta_{ad}$ =0.156 and the sample bias was 1.1 V. (b) An STM image after exposed to 1.3 L D<sub>2</sub>O at 300 K (135 $\times$ 135 Å<sup>2</sup>).  $\theta_{ad}$ =0.316 and the sample bias was 1.5 V. The asterisks indicate the adatoms that cannot be explained by the previous adatom-rest atom-pair reaction model. (c) Percentages of the reacted adatoms that are incompatible with the model as a function of  $\theta_{ad}$ . (d) Numbers of the reacted adatoms per 100 unit cells as a function of the number of the neighboring reacted adatoms. The experimental results (squares) are compared to the simulation (circles) in which no correlation was considered between the reactants. A thousand unit cells were analyzed in each case.

$\theta_{ad}$ =0.156 in the experiment and calculation, respectively, which shows the presence of an attractive interaction between the reactants.

The reaction products were investigated using EELS (Fig. 4). After exposure to 0.01 L H<sub>2</sub>O [spectrum (a)], the Si-OH bend and/or stretch modes were observed at 92 and 108 meV,<sup>3</sup> which is superimposed by a broad loss at  $\sim$ 100 meV. The SiO-H stretch peak was observed at 456 meV.<sup>3</sup> The broad feature is ascribed to the libration modes of a condensed water molecule, that also gives peaks at 205 and  $\sim$ 430 meV due to scissors and H-bonded OH stretch, respectively. With increasing exposure (0.54 L), condensed water becomes dominant [spectrum (b)]. After the surface was heated to 300 K, the condensed water disappeared and losses due to Si-H stretch were observed at 257 and 265 meV [spectrum (c)].

The clean surface was exposed to 30 L H<sub>2</sub>O at 300 K and then EELS was recorded at 82 K [spectrum (d)], which corresponds to the STM results at 300 K (Fig. 3). The SiO-H stretch peaks appear at 456 meV in both (c) and (d), suggesting a similar configuration of the hydroxy species. A notable feature is the Si-H stretch mode with only one peak at 257 meV. This is in contrast to the spectrum (c), where two

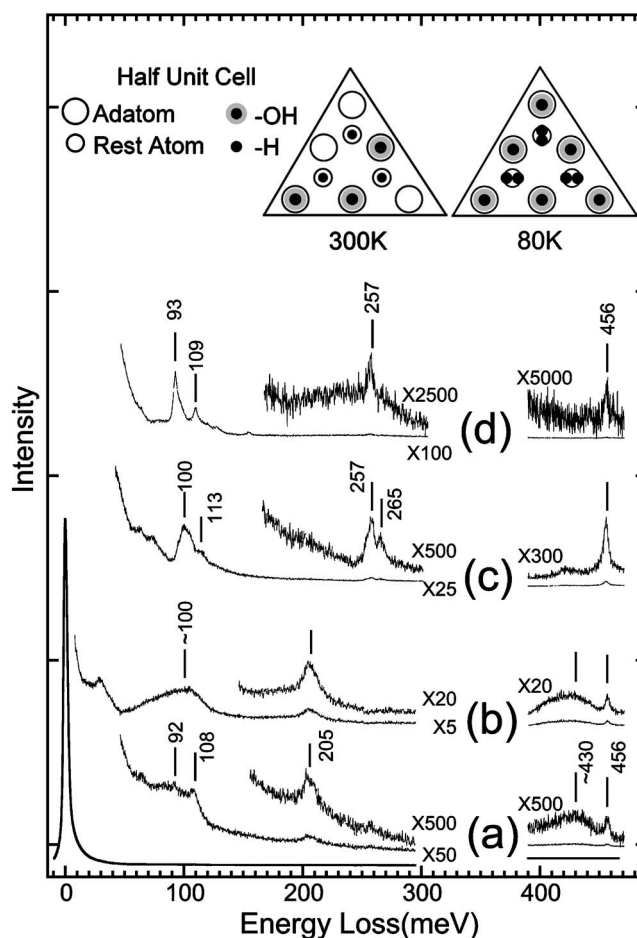


FIG. 4. EELS spectra of Si(111)-(7 $\times$ 7) recorded after exposed to (a) 0.01 L and (b) 0.54 L H<sub>2</sub>O at 82 K. The spectrum (c) was recorded after the surface (b) was heated to 300 K and then cooled to 82 K. The spectrum (d) was recorded after exposed to 30 L of H<sub>2</sub>O at 300 K and then cooled to 82 K. The inset shows schematic models of the reaction products at 300 K (left) and 80 K (right).

distinct peaks at 257 and 265 meV are observed. The 257 and 265 meV peaks were assigned to the monohydride (Si-H) and dihydride (Si-H<sub>2</sub>) species, respectively.<sup>11,12</sup> Therefore, the EELS indicates that the dihydride formation is promoted at 82 K.

#### IV. DISCUSSION

A Si(111)-(7 $\times$ 7) surface has a unit cell that is composed of two half cells: one has a stacking fault and the other does not. It is known that the faulted half cell has slightly higher local density of states than the other. The reaction of water at room temperature occurs with little preference of the half cells, which implies that electronic states of the substrate are not so much responsible for the reaction. On the other hand, the reaction occurs preferentially at the center adatom compared to the corner adatom by a factor of 2–4. This result implies that the partial dissociation occurs across the adatom-rest atom pair since the center adatom has two neighboring rest atoms, whereas the corner adatom has one.<sup>6,7</sup>

This hypothesis indicates that the local coverage of the reacted adatoms does not exceed 0.5 because the number of rest atoms is half of that of the adatoms. It was, however, pointed out by Self *et al.*<sup>7</sup> that half unit cells that involved more than three reacted adatoms exist at high coverage. The room-temperature experiment in the present study also indicates that 3% of the total half unit cells involves more than three reacted adatoms at  $\theta_{ad}=0.156$ . The contradiction is more obvious at 78 K, where the reacted adatoms form two-dimensional islands, i.e.,  $\theta_{ad}$  is locally unity. Based on the EELS result, we modify the adatom-rest atom-pair reaction mechanism and propose that dihydride species is formed at the rest-atom sites, enabling more than half of the adatoms to be involved in the reaction. This reaction model is schematically shown in the inset of Fig. 4. The dihydride is minority species at 300 K and thus was not detected by EELS. We note that dihydride species is formed on Si(111) by the reaction with atomic hydrogen at 300 K, although it requires  $\sim 100$  L exposure.<sup>13,14</sup>

The STM showed unstable features on the depressed areas [Fig. 2(a)], which disappeared after the surface was heated to 300 K [Fig. 2(c)]. According to the EELS result, we ascribe the unstable features to condensed state of water. The unstable imaging suggests its insulating property, which is in line with the assignment. The results indicate that the reaction is mediated via molecular precursor state and the aggregation is caused by an attractive interaction. This is compatible with the STM result at 300 K suggesting the presence of an attractive interaction between the reactants [Fig. 3(d)]. The origin of the attractive force was studied in terms of density-functional theory,<sup>15</sup> which suggests the hydrogen bonding between the reactants as a candidate. We infer that

the reaction (dissociation) probability of the precursor is low on the clean surface at 80 K so that it is stabilized via hydrogen bonding with the hydroxy group at the reacted sites. The dihydride formation is kinetically favorable due to the aggregation, whereas it needs to break the Si-Si back bonds and thus is energetically unfavorable compared to the formation of two monohydride species.

It is interesting to compare the present result to the case of Si(100)-(2 $\times$ 1), where dissociated H and OH species bond to Si adatoms in the same or adjacent dimer of the (2 $\times$ 1) reconstructed surface.<sup>16,17</sup> An attractive interaction, possibly due to hydrogen bonding,<sup>15</sup> caused island formation of the reacted species.<sup>18</sup> Infrared absorption spectra,<sup>19</sup> however, indicated no presence of dihydride species at 80 K; the unit cell (dimer) can accommodate both the OH and H species with no dangling bond remained and all dangling bonds can be consumed without dihydride configuration. Therefore, the dihydride formation is ascribed to the characteristic structure of Si(111)-(7 $\times$ 7), which has twice as many dangling bonds at the adatom sites as those at the rest-atom sites.

## V. CONCLUSION

In summary, the reaction of water with Si(111)-(7 $\times$ 7) was investigated by means of STM and EELS at 80 K. At the initial reaction stage, partially dissociative adsorption proceeds, forming Si-OH and Si-H species. We observed two-dimensional islands of the dissociated species, and the feature of molecular adsorption. We modify the adatom-rest atom-pair reaction mechanism and propose that dihydride species is formed at the rest-atom sites, enabling more than half of the adatoms to be involved in the reaction.

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